

# **C-E ENVIRONMENTAL, INC.**

C-E Environmental-FR-89  
Project No. 51155

## **FINAL REPORT**

**SOUTHERN CALIFORNIA AIR QUALITY STUDY SAMPLER CHEMISTRY**

**Contract No. A5-186-32**

**Prepared for**

**California Air Resources Board  
P. O. Box 2815  
Sacramento, CA 95812**

**by**

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**COMBUSTION ENGINEERING**

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## ABSTRACT

This document describes the analytical methods and sampling media employed to measure the ambient concentrations of selected gases and chemically speciated components of the fine and PM-10 aerosol species for the Southern California Air Quality Study (SCAQS) at nine sites during 17 moderate to high PM-10 and/or O<sub>3</sub> days in the summer and fall of 1987. Also included in this document is a description of QC/QA procedures that were employed and data flags that were used for flagging suspect data. Analytical detection limits, site and/or seasonal dependent blanks, and analytical precision values for all the different analytes have been calculated and are summarized in this document. Samples were collected at each site using the specially designed SCAQS sampler during five intervals each day to derive temporal relationships for the different air pollutant of interest. Samples were collected by AeroVironment (AV) and then shipped to EMSI where they were distributed to different analytical laboratories for chemical analyses. Analytical results for samples, dynamic field blanks and duplicate analyses were submitted to ENSR, ARB's data management contractor, where they have been combined with field data including sample volumes supplied by AV, to calculate blank corrected concentrations for all the species of interest.

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Finally, we wish to acknowledge the support and guidance of Eric Fujita of the California Air Resources Board who served as our project officer.

This report was submitted in fulfillment of ARB Agreement NO. A5-187-32, entitled "Southern California Air Quality Study: Sample Analyses and Reporting" by EMSI, C-E Environmental, Inc., under the sponsorship of the California Air Resources Board. Work was completed as of 30 September 1988.

## PROJECT SUMMARY

An integrated gas and aerosol sampler built and designed by AeroVironment, Inc. (AV) was used to collect ambient samples for analysis at eight sites in the South Coast Air Basin (SCAB) and one background site offshore as part of the Southern California Air Quality Study (SCAQOS). AV field technicians operated these samplers at nine sites for eleven moderate to high PM-10/O<sub>3</sub> days in the summer of 1987 as well as at six sites for an additional six days during the winter of 1987. Sampling consisted of taking five sets of samples per day on filters, impregnated filters and coated "denuder" tube media for the following chemical species:

- o total suspended nitrate
- o sulfur dioxide
- o fine particulate nitrate
- o nitric acid
- o ammonia
- o fine particulate ammonium
- o fine and PM-10 mass
- o fine and PM-10 ionic species ( $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{=}$ )
- o PM-10 sodium (by atomic absorption)
- o fine and PM-10 organic carbon and elemental carbon, corrected for artifacts
- o fine and PM-10 elements (by X-ray fluorescence)
- o b-absorption by fine particulate species

ENSR analyzed the samples for organic and elemental carbon; NSI Technology Services Corporation analyzed the samples for elements; and U.C. Davis (and later Radiance Research) analyzed the samples for b-absorption. C-E Environmental, Inc. (EMSI) analyzed the samples for the remainder of the analytes listed above.

EMSI procured and prepared all sampling media for the SCAQS samplers. Random samples were submitted to the other analytical laboratories prior to the start of the actual sampling period to check for acceptable background levels. EMSI prepared and packaged the filter and denuder



media in sampling kits and then shipped them in six shipments to AV's headquarters in Monrovia, CA where they were later distributed to each site. Exposed samples and dynamic field blanks were refrigerated at each site and then returned to EMSI in ice chests containing "blue-ice" packets via AV's headquarters. Samples were logged in at EMSI and then distributed (along with the field data sheets) to the appropriate laboratory for analysis.

Dynamic field blanks, representing approximately 10% of the total number of samples collected, were employed at each site for this study in order to correct the sample filters for blank levels of the species of interest. Duplicate analyses of approximately 5% of the total number of samples collected provided the data necessary to calculate analytical precision for each sample analyzed. Sample volume uncertainties were calculated for each sample by AV based on sample flow rate uncertainties and submitted to ENSR, ARB's data management contractor. Analytical results were subjected to both internal and external audits and submitted to ENSR who (a) combined field data and analytical results from different sources to calculate blank corrected concentration data, (b) calculated overall uncertainties for each sample, and (c) performed a series of validation checks on the merged data base.

A total of 675 sets of SCAQS samples plus 63 sets of blanks were collected as scheduled for this program. Each set comprised an ammonia denuder tube and 13 filters. Thus, if there had been no missing samples, the program would have generated 10,332 samples (738 sets x 14 samples per set). Several power failures and several instances where filter cassettes were not attached to the sampling inlet accounted for a loss of 126 samples. In addition, damaged and contaminated samples accounted for 130 potentially invalid samples, 32 samples were lost or mislabelled in transit and/or storage between sampling and analysis, 65 samples were lost due to use of incorrect filter media, 34 samples are suspect due to flow rate problems, 77 samples are suspect due to analytical problems, 33 blank samples are suspect due to extremely high blank levels, and 18 samples are suspected of transcription errors. In summary, out of a total of 10,332 samples that were to be collected for this program, 515

samples were missing or suspected of validity problems. Thus, the valid data capture rate for the SCAQS samplers was 95% through Level 1 validation. Level 2 validation, to be performed by ENSR, is expected to reduce this value slightly.

ENSR is currently compiling the SCAQS sampler data base, which will include the blank corrected concentrations plus the overall uncertainty for each analyte for every sample. ENSR will document the methods used to process and validate the data. The final data base is scheduled for release to the public by late spring 1989 and can be obtained from the ARB (Bart Croes, 916-323-1534).

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## 1.0 INTRODUCTION

The Southern California Air Quality Study (SCAQS) was an integrated air quality study whose primary objective was to develop a comprehensive and fully documented air quality and meteorological database for the South Coast Air Basin (SCAB). This database will be used to test, evaluate and improve elements of air quality simulation models for oxidants, PM-10, fine particles, toxic air contaminants and acidic species. The overall program has been described in detail in the SCAQS program plan (Sonoma Technology, Inc., 1986).

This report describes the analytical measurements made on samples collected at nine sites (designated as Type B sites in the program plan) using an integrated gas and aerosol sampler specially designed and built for this program by AeroVironment, Inc. which is referred to as the SCAQS sampler. A complete description of this SCAQS sampler, including the design and testing of the prototype samplers, is presented in AeroVironment's Final Report #87/649 submitted to the California Air Resources Board (AeroVironment Inc., 1988). The SCAQS sampler consisted of three components, each running off a separate pump. A schematic of the sampler is shown in Figure 1-1. Collection methods and subsequent analytical methods for different analytes are summarized in Table 1-1.

Component #1 was designed basically to measure gaseous concentrations and consisted of the following five sampling legs mounted in parallel under a rainshield with legs #3, #4 and #5 located behind a Teflon coated AIHL designed low volume flowrate cyclone to remove particles larger than 2.5  $\mu\text{m}$  mass median aerodynamic diameter:

- o Leg #1: Open face Teflon prefilter plus backup nylon filter in a Teflon filter holder to collect total nitrate (including nitric acid);
- o Leg #2: Open face filter pack, consisting of a Zefluor Teflon prefilter and a sodium carbonate impregnated cellulose ester fiber filter in a two-stage Teflon filter holder to collect sulfur dioxide;



TABLE 1-1  
SUMMARY OF SCAQS SAMPLER COLLECTION AND ANALYTICAL METHODS

Species	Collection Method	Analysis Methods
<u>Gases and Total Particles</u> (Open-faced collectors beneath a rain shield)		
Nitrate	Nylon filter*	IC for $\text{NO}_3^-$
$\text{SO}_2$	$\text{Na}_2\text{CO}_3$ /Glycerine-impregnated Whatman No. 541 cellulose filter behind a Zefluor Teflon prefilter	IC for $\text{SO}_4^{=}$
<u>Gases and Volatile Fine Particles</u> (Collectors behind Teflon-coated AIHL cyclone)		
$\text{HNO}_3/\text{NO}_3^-$	Denuder difference method using a pair of nylon filters,* one behind an $\text{MgO}$ -coated denuder tube to remove $\text{HNO}_3$	IC for $\text{NO}_3^-$
$\text{NH}_3/\text{NH}_4^+$	Oxalic acid-coated denuder tube for $\text{NH}_3$ plus backup quartz filter impregnated with oxalic acid	Colorimetry for $\text{NH}_4^+$ for denuder tubes and backup filters
<u>Fine Particles</u> (Collectors behind Sensidyne Model 240 cyclone)		
Organic and Elemental Carbon	Quartz filter	Dual temperature zone furnace oxidation
Mass/trace elements	Teflo Teflon Filter	Mass by gravimetry; elements by XRF/NAA
$\text{SO}_4^{=}$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{NH}_4^+$	Teflo Teflon filter	Anions by IC; $\text{NH}_4^+$ by colorimetry; Na by AA
b-absorption	Nuclepore filter	Integrating plate
<u>PM-10 Particles</u> (Collectors behind GMW-254-1 PM-10 Inlet)		
Organic and Elemental carbon	Quartz filter	Dual temperature zone furnace oxidation
Mass/trace elements	Teflo Teflon filter	Mass by gravimetry; elements by XRF
$\text{SO}_4^{=}$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{NH}_4^+$ , Na	Teflo Teflon filter	Anions by IC; $\text{NH}_4^+$ by colorimetry; Na by AA

\* Topped by a Zefluor Teflon prefilter to prevent particles from plugging up the nylon filter.

- o Leg #3: Teflon pre-filter plus backup nylon filter in an in-line aluminum filter holder located behind a magnesium oxide coated nitric acid denuder to collect PM-2.5 nitrate;
- o Leg #4: Teflon pre-filter plus backup nylon filter in an in-line Teflon filter holder to collect PM-2.5 nitrate and nitric acid; and
- o Leg #5: Oxalic acid coated denuder to collect ammonia plus a backup oxalic acid impregnated quartz fiber filter in an in-line aluminum filter holder to collect PM-2.5 ammonium.

Component #2 was designed to measure the fine (i.e. PM-2.5) particulate composition. A total of four sampling legs in parallel series located behind a medium volume flowrate Sensidyne Model 240 cyclone were used to collect the following fine particulate species:

- o Leg #6: Nuclepore polycarbonate filter in an in-line aluminum filter holder to measure PM-2.5 b-absorption;
- o Leg #7: Quartz filter in an in-line aluminum filter holder to collect PM-2.5 carbonaceous species;
- o Leg #8: Pre-weighed Teflon filter in an in-line aluminum filter holder to measure PM-2.5 mass and elements; and
- o Leg #9: Teflon filter plus a backup quartz filter in an in-line aluminum filter holder to measure PM-2.5 ionic species and the organic carbon artifact, respectively from the two filters.

Component #3 was built to measure the PM-10 particulate composition and consisted of three legs in parallel mounted behind a medium volume flow rate General Metal Works Model 254-I 10  $\mu$ m inlet to collect the following species:

- o Leg 10: Quartz filter in an in-line aluminum filter holder to measure PM-10 carbonaceous species;
- o Leg 11: Pre-weighed Teflon filter in an in-line aluminum filter holder to measure PM-10 mass and elements; and
- o Leg 12: Teflon filter in an in-line aluminum filter holder to measure PM-10 ionic species plus sodium.



Based on the results of the prototype SCAQS sampler testing, the sampler received minor modifications to improve collection efficiency for the species of interest. In its final design configuration, the SCAQS sampler demonstrated the following properties:

- o Equivalency of all ten SCAQS samplers built for the study;
- o Equivalency of sampling legs for the PM-2.5 fraction; likewise for the PM-10 fraction;
- o High SO<sub>2</sub> collection efficiency (> 95%);
- o Low nitric acid loss in cyclone and sampling lines (<5%);
- o High efficiency for oxalic acid coated denuder for ammonia (>90%) and backup oxalic acid impregnated quartz filter for PM-2.5 ammonium (>99.9%);
- o The average coefficient of variation for blank corrected mass determinations based on twelve separate sampling periods using Teflon filters in all legs of the prototype sampler was less than 7% for total suspended particles (i.e. legs 1 and 2), less than 6% for PM-2.5 aerosol (i.e. legs 3, 4, 7, 8, and 9), and less than 3% for PM-10 aerosol (i.e. legs 10,11 and 12);
- o The average PM-10 mass determinations made with the prototype SCAQS sampler (i.e. legs 10, 11 and 12) using three separate in-line filter holders in parallel behind the PM-10 inlet agreed to better than 1% with that of a collocated PM-10 sampler using a single open-face filter holder behind a PM-10 inlet which indicates no loss in the flow splitter used with the SCAQS sampler for sampling PM-10 aerosol; and
- o The coefficient of variation for nitric acid collected on two separate nylon filters (i.e. legs 3 and 4 without the in-line nitric acid denuder) downstream of a single Teflon pre-filter to remove particulate nitrate was 3%.

A summary of the results for the ten collocated SCAQS samplers operated during ten separate side-by-side pre-study evaluations is presented in Table 1-2. Because of the unusually clean air in Monrovia, California during the side-by-side evaluation testing, the filter loadings for many of the low volume flowrate samples were often near their overall detection limit (i.e. defined as three times the dynamic blank

TABLE 1-2

## SUMMARY OF SIDE-BY-SIDE EVALUATION OF TEN COLLOCATED SCAQS SAMPLERS

Leg	Species	Typical Concentration for the SCAB ( $\mu\text{g}/\text{m}^3$ )	Mean Concentration for the Evaluation ( $\mu\text{g}/\text{m}^3$ )	Mean Coefficient of Variation* %
1	Total $\text{NO}_3^-$	10	5	9
2B	$\text{SO}_2$ as $\text{SO}_4^{=}$	15	1	21
3	PM-2.5 $\text{NO}_3^-$	8	3	7
4	$\text{HNO}_3$ + PM-2.5 $\text{NO}_3^-$	21	4	11
5F	$\text{NH}_3$ as $\text{NH}_4^+$	3	1	42
5B	PM-2.5 $\text{NH}_4^+$	5	4	30
6	PM-2.5 $b_{\text{abs}}$	200 +	40 +	20
7	PM-2.5 OC	15	1	9
	PM-2.5 EC	2	1	25
8	PM-2.5 Mass	40	40	8
	PM-2.5 S	0.5	2	5
9F	PM-2.5 $\text{Cl}^-$	3	0.1	43
	PM-2.5 $\text{SO}_4^{=}$	5	5	6
9B	Organic Artifacts	3	6	10
10	PM-10 OC	20	13	10
	PM-10 EC	4	2	20
11	PM-10 Mass	50	60	5
	PM-10 Fe	2	2	9
12	PM-10 $\text{Cl}^-$	5	0.7	11
	PM-10 $\text{SO}_4^{=}$	5	6	7

\* Mean coefficient of variation is the mean of the coefficients of variation for each period.

+ Units  $10^{-6} \text{ m}^{-1}$

variability), which resulted in relatively high coefficients of variation. For those sampling periods with concentrations more typical of those for the South Coast Air Basin (SCAB), the coefficients of variation of most analytes was a more acceptable 5-10%. One exception was  $b_{abs}$  with an average coefficient of variation of 20% presumably due to a large variation in the initial absorbance of the different Nuclepore polycarbonate filters used for this study. The other exceptions were ammonia from the oxalic acid-coated denuder (leg #5F, where F designates front) and PM-2.5 ammonium ion from the oxalic acid impregnated filter (leg #5B, where B designates back) which showed large coefficients of variation (20-30%). This was later attributed to loose or missing ferrules for the ammonia denuder (i.e. leg #5A) in front of the oxalic acid impregnated filters (i.e. leg #5B); see AeroVironment 1988 for details.

C-E Environmental Inc. (EMSI) was chosen by the California Air Resources Board (CARB) to oversee and coordinate all analyses involving the SCAQS sampler. EMSI procured and prepared all sampling media, packaged the sampling supplies into discrete sampling kits and shipped them to AeroVironment (AV) who in turn delivered the individual kits to each of the nine sites.

Sampling commenced in June 1987 and continued on an episodic basis for a total of eleven days at nine sites during the summer of 1987 and then for a total of six days at six sites during the winter of 1987 on a schedule of five sampling periods per day. Details of the routine sampling operations for the SCAQS sampler are presented in the SCAQS B-Site Station Operations Manual (AeroVironment, 1987) whereas a discussion of the daily sampling is presented in AV's final report on field operations for the 1987 SCAQS study (AeroVironment, 1989).

The specific sampling dates and B-sites involved in the 1987 SCAQS study are summarized in Table 1-3. The only exception to the five sampling periods per day was for the collection of ammonia with an oxalic acid coated denuder tube (and fine particulate ammonium on the backup filter behind the denuder) at the remote offshore site on San Nicolas Island

TABLE 1-3

## SCAQs B-SITE SAMPLING NETWORK SITES AND SAMPLING SCHEDULE\*

Day #	Sampling Date	Julian Date	1	2	3	4	5	6	7	8	9
			Anaheim	Azusa	Burbank	Claremont	Downtown Los Angeles	Hawthorne	Long Beach	Rubidoux	San Nicolas Island
1	6/19/87	170	x	x	x	x	x	x	x	x	x
2	6/24/87	175	x	x	x	x	x	x	x	x	x
3	6/25/87	176	x	x	x	x	x	x	x	x	x
4	7/13/87	194	x	x	x	x	x	x	x	x	x
5	7/14/87	195	x	x	x	x	x	x	x	x	x
6	7/15/87	196	x	x	x	x	x	x	x	x	x
7	8/27/87	239	x	x	x	x	x	x	x	x	x
8	8/28/87	240	x	x	x	x	x	x	x	x	x
9	8/29/87	241	x	x	x	x	x	x	x	x	x
10	9/2/87	245	x	x	x	x	x	x	x	x	x
11	9/3/87	246	x	x	x	x	x	x	x	x	x
12	11/11/87	315	x	x	x	x	x	x	x	x	x
13	11/12/87	316	x	x	x	x	x	x	x	x	x
14	11/13/87	317	x	x	x	x	x	x	x	x	x
15	12/3/87	337	x	x	x	x	x	x	x	x	x
16	12/10/87	344	x	x	x	x	x	x	x	x	x
17	12/11/87	345	x	x	x	x	x	x	x	x	x

\* Five sampling periods per day: (a) Summer (Days #1 - #11): 0100-0600 PDT, 0600-1000 PDT, 1000-1400 PDT, 1400-1800 PDT, 1800-0100 PDT; (b) Winter (Days #12 - #17): 0000-0600 PST, 0600-1000 PST, 1000-1400 PST, 1400-1800 PST, 1800-0000 PST; (c) Exception: San Nicolas Island for Days #7 - #11 when field technician combined sampling periods for ammonia and fine particulate ammonium (i.e. leg #5 of SCAQS sampler) to improve detection for these species.

TABLE 1-4

SAMPLING SCHEDULE FOR AMMONIA AT SAN NICOLAS ISLAND  
DURING AUGUST-SEPTEMBER 1987

---

<u>Julian Date</u>	<u>Start Time (PDT)</u>	<u>End Time (PDT)</u>
239	0100	1000
	1000	1800
	1800	0600
240	0600	1400
	1400	1800
	1800	0100
241	0100	0600
	0600	1400
	1400	1800
	1800	0100
245	0100	1000
	1000	1800
	1800	0600
246	0600	1400
	1400	0100

---

during August and September. During this time period, the ammonia denuder tubes and backup filters for fine particulate ammonium were used to sample ambient air less frequently than five times a day. The specific time periods are summarized in Table 1-4. Unfortunately, the records for several of the ammonia denuders and backup filters for these periods was poorly documented and consequently the results for several samples were lost.

Subsequent sections of this document will address the following topics:

- o preparation of sampling media;
- o sampling kits and sample collection logistics;
- o analysis methods;
- o quality control and quality assurance audits;
- o data reduction and reporting procedures; and
- o SCAQS sampler results.

## 2.0 SUBSTRATES AND SUBSTRATE PREPARATION

The following section will describe the various sampling media substrates used in the SCAQS samplers as well as the preparation of these substrates.

### 2.1 SUBSTRATES

All filters used for this program were ordered from the different filter manufacturers with the specification that all filters be from the same lot number. Details on the specific filters used for this program are summarized on Table 2-1. In addition to the filters procured by EMSI and ERT (quartz filters for carbon), AeroVironment supplied MgO-coated nitric acid denuders (i.e. one 10-tube array per sampler since they were recycled for every sampling period) and approximately 600 uncoated denuder tubes for ammonium collection. These latter denuder tubes were coated by EMSI for the summer study and then recycled for the fall study (after recoating).

The following substrates were used in the various sampling legs of the SCAQS sampler (see Figure 1-1 for schematic of the sampler):

- o Nylon filter plus a ringed Teflo Teflon prefilter to reduce plugging the nylon filter in legs #1, #3 and #4; these filter pairs were designated as 1-N1, 3-N2 and 4-N3 respectively in the final substrate numbering scheme;
- o Sodium carbonate impregnated Whatman No. 541 cellulose ester fiber filter with a Zefluor Teflon prefilter to remove particulate sulfate in leg #2; these filters were designated as 2B-C1 and 2F-Z1 respectively, where "B" stands for backup filter and "F" stands for front filter;
- o Oxalic acid coated denuder tube in leg #5, designated as 5F-D1, followed by an oxalic acid impregnated quartz filter, designated as 5-X1;
- o Polycarbonate membrane filter in leg #6, designated as 6-P1;

TABLE 2-1  
FILTERS USED IN SCAQS SAMPLER

Filter Type	Manufacturer	Catalog #	Lot #
0.65 $\mu$ m pore Nylon	Sartorius	11905.047N	3110506575-8
2 $\mu$ m pore Teflo Teflon	Gelman	R2PJ047	2089
2 $\mu$ m pore Zeflour Teflon	Gelman	P5PJ047	761652
Cellulose Ester, No. 541	Whatman	1541047	6011
0.4 $\mu$ m pore Polycarbonate	Nuclepore	28157-960	81B4A
Quartz	Pallflex	2500QA0UP	6257-G



- o Quartz filter in legs #7, #9 (backup filter) and #10, designated as 7-Q1, 9B-Q2, and 10-Q3 respectively;
- o Preweighed ringed Teflo Teflon filter in legs #8 and #11, designated as 8-T1 and 11-T3 respectively; and
- o Teflo Teflon filter in legs #9 and #12, designated as 9F-T2 and 12-T4 respectively.

## 2.2 SUBSTRATE PREPARATION

All filters were inspected prior to use for visual pin holes, creases or tears and were rejected if necessary. Blanks were analyzed at random for different filters to check background levels for the analytes of interest. All filter lots were found to be acceptable. Several of the filters were used as is without further preparation; they include the nylon filters plus the Teflo Teflon pre-filters used in legs #1, #3 and #4, the Zefluor Teflon prefilter used with the carbonate impregnated filter in leg #2, and the Teflo Teflon filters used in legs #9 and #12 for ionic species. The other substrates required preparation prior to use in the field. The steps involved with each substrate are described below.

### 2.2.1 Preparation of Carbonate Impregnated Filters Used to Collect SO<sub>2</sub>

- o Transfer 215 g Na<sub>2</sub>CO<sub>3</sub> into 1 liter volumetric flask. Add 100 ml glycerine and fill to volume with DI water. Mix until completely dissolved.
- o Pour 200 ml of the Na<sub>2</sub>CO<sub>3</sub>-glycerine solution into a large beaker and place up to 50 47mm diameter Whatman No. 541 cellulose ester filters in the solution to soak.
- o Remove one filter at a time from the beaker with forceps and place in a fritted Buchner funnel. Pull a vacuum on the filter for 1 minute to remove excess liquid.
- o Place each filter in a plastic petri dish and then store petri dishes in a zip-lock bag in a refrigerator until ready to make up filter kits for the field.

### 2.2.2 Preparation of Oxalic Acid Impregnated Filters Used to Collect $\text{NH}_4^+$

- o Dissolve 7.0 g fresh oxalic acid in 200 ml ethanol. (Scrape off top layer of solid oxalic acid and discard before weighing out desired amount.)
- o Place each 47 mm diameter quartz filter in the bottom of a plastic petri dish and spike each filter with 1 ml of the oxalic acid solution with an Eppendorf pipette, making sure to wet entire filter.
- o Place several paper towels spiked with the oxalic acid solution in the bottom of a large vacuum dessicator and stack up to 50 impregnated filters in the open petri dishes on top of the paper towels.
- o Place the dessicator under vacuum for 2 hours to evaporate the ethanol. (An oil trap is needed in-line before the vacuum pump to prevent ethanol reaching the pump.)
- o Place the lid on each petri dish and seal the petri dish with parafilm.
- o Place each group of impregnated filters in a zip-lock bag along with a couple of oxalic acid impregnated paper towels to trap any ambient ammonia and store in a refrigerator until ready to make up filter kits for the field.

### 2.2.3 Preparation of Oxalic Acid Coated Denuder Tubes Used to Collect Ammonia

- o The denuder tubes were prepared by AV by cutting 4' lengths of 3 mm ID glass tubing in half and mounting the glass tube inside a 1" diameter PVC pipe. A mark was made with tape 15 cm from one end. This section of the glass tubing is not treated, coated or extracted; it is used to laminarize the incoming air flow during sampling.
- o Etch each denuder tube with concentrated HF by drawing HF up to the taped mark with a 10 ml plastic syringe and then drain the tube after 5 minutes. Rinse the tube in a similar manner four times with DI water and dry the tube with helium that has been passed through an oxalic acid coated filter to remove ammonia.
- o Dissolve 1.06 g fresh oxalic acid in 95 ml spectrograde methanol and 5 ml reagent grade glycerol.
- o Coat each tube with oxalic acid solution by drawing up to the 15 cm mark with a 10 ml plastic syringe and then drain tube immediately. With the tube held in a vertical position, use

ammonia-free helium to dry the coated tube for 5 minutes. Immediately seal the ends of the tube with parafilm and place PVC end caps over the 1" diameter PVC pipe.

#### 2.2.4 Pre-weighing Teflo Teflon Filters Used to Measure Mass and Elements

All filter weighing took place in a temperature and humidity controlled clean room where temperature and relative humidity are recorded continuously. The Teflo Teflon filters were equilibrated for a minimum of 24 hours at a temperature of  $25 \pm 2^{\circ}\text{C}$  and a relative humidity of  $45 \pm 5\%$  RH and then weighed on a Mettler microbalance with a sensitivity of 1.0  $\mu\text{g}$ . Weighed filters were placed in petri dishes, assigned a unique ID number and the filter IDs and filter weights were logged into a notebook with columns for the dates of filter weighing, the initial weights (and the final weights after sampling) as well as the name of the technician.

The balance was checked with a 2.0 mg Class M weight at the beginning of each session. Several QC 47 mm diameter Teflo Teflon filters were checked every 20 filters. If the QC filters were within 15  $\mu\text{g}$  of their nominal values, weighing continues. If they were more than 15  $\mu\text{g}$  from their nominal values, the balance was rechecked with the 2.0 mg class M weight and all filters weighed since the previous check were reweighed. After each weighing session, ten percent of all filters in the batch were reweighed by another technician. If any reweight exceeded the previous weight by more than 15  $\mu\text{g}$ , another ten percent were reweighed. This reweighing continued until all reweights passed the 15  $\mu\text{g}$  test. Weights were written on a data sheet and entered into computer files for data processing.

#### 2.2.5 Preparation of Polycarbonate Filters Used to Measure b-absorption

For the summer study, only five percent of the polycarbonate filters were analyzed by U.C. Davis prior to the field study to record an initial absorbance value since the blank filters used in the prototype sampler

testing indicated minimal variability in b-absorption ( $b_{abs}$ ). However, it became obvious after receiving the  $b_{abs}$  data from the summer study, that there were problems with this data which were either caused by the analytical methodology employed by U.C. Davis to measure  $b_{abs}$  or that the variability in absorbance for the blank filters was higher than anticipated. Thus, for the winter study period, every polycarbonate filter was measured for its individual initial absorbance using a modification of the integrating opal plate absorbance methodology pioneered at the University of Washington (Lin et al 1973).

In addition to the b-absorption measurements made by U.C. Davis, Radiance Research, under the supervision of Mr. Ray Weiss, analyzed the same polycarbonate filters. Radiance was contracted for the measurements by CARB after the field sampling had occurred and no prior optical tare measurements could be done on the individual filters. Because of the lack of reference measurements and the excessive variability in the transmittance of the blank filters, a spectrophotometer was developed to measure the transmittance tare from the unsampled edge of each filter (Weiss, 1988). The modification involved using a narrow angle fiber optic source/receiver with diffuser and neutral density (ND) filter to implement the integrating plate technique. Since the substrate edge for each filter served as the tare measurement for that sample, the problems with having no prior measurements and excessive blank variability were eliminated and reliable optical absorption measurements were obtained. Consequently, no filter preparation was needed using this technique.

#### 2.2.6 Preparation of Quartz Filters Used to Collect Carbonaceous Species

ENSR prefired the Pallflex quartz filters used to collect carbonaceous aerosol species to 700°C in air for two hours to reduce the organic carbon and elemental carbon blank levels prior to use for the SCAQS study. Filters were heated ( in batches of 200) in a porcelain crucible inside a muffle furnace, then removed and placed in individual petri

dishes and delivered to EMSI for inclusion in the sampling kits for the field.

## 2.3 PRE-STUDY TESTS OF SUBSTRATES

Pre-study tests of substrates for the SCAQS sampler were conducted to provide information on blank values and sampling efficiency. The results of these pre-study prototype sampler testing are summarized below.

### 2.3.1 Substrate Blank Results

Dynamic blank results for analytes of interest are summarized in Table 2-2. These results are based on an average of ten of each substrate used in a series of prototype SCAQS sampler tests conducted at AV's headquarters in Monrovia, CA prior to the SCAQS study. Generally, the results for the dynamic blanks were only slightly higher than that of laboratory blanks that remained in the laboratory in covered petri dishes. Part of this difference is due to contamination as a result of handling the dynamic field blanks in the field and part of this is due to the fact that in several cases ambient air was pulled through the dynamic field blanks loaded in the SCAQS samplers during a nominal 4-hour period for a nominal 10 minutes while the site technician was checking sampler flow rates. Differences of a factor of 2-3 between laboratory blanks and dynamic field blanks were observed for nitrate on nylon filters, for ammonium on oxalic acid coated denuder tubes and oxalic acid impregnated quartz filters, and for organic carbon on quartz filters. These results led to the requirement that dynamic field blanks be taken frequently from each site during the SCAQS study and that all site technicians received adequate training in handling the different SCAQS sampler substrates. This training included checking that the petri dishes containing exposed filters had been resealed tightly and using parafilm to re-seal the petri dishes containing the oxalic acid impregnated filters and the ends of the ammonia denuder tubes. Parafilm was also used to seal the lids of the plastic boxes holding the petri dishes with exposed filters.

TABLE 2-2

## SUMMARY OF DYNAMIC BLANK RESULTS FOR SCAQS SAMPLER SUBSTRATES

LEG #	SUBSTRATE	ANALYTE	DYNAMIC BLANK (5g/substrate)	
			$\bar{x}$	$\sigma$
1,3,4	Nylon	$\text{NO}_3^-$	3.2	0.5
2B	Carbonate impregnated cellulose	$\text{SO}_2$ as $\text{SO}_4^{=}$	0.8	0.2
5F	Oxalic acid coated denuder	$\text{NH}_3$ as $\text{NH}_4^+$	0.5	0.2
5B	Oxalic acid impregnated Quartz	$\text{NH}_4^+$	0.6	0.3
6	Polycarbonate	$b_{\text{abs}}$	39*	32*
7,10	Quartz	Organic Carbon	15.0	6.7
7,10	Quartz	Elemental Carbon	0.9	0.8
8,11	Teflon	Mass	40	36
8,11	Teflon	S (by XRF)	0.1	0.3
8,11	Teflon	Fe (by XRF)	0.4	0.1
9,12	Teflon	$\text{NH}_4^+$	0.4	0.2
9,12	Teflon	$\text{Cl}^-$	0.5	0.2
9,12	Teflon	$\text{NO}_3^-$	2.0	1.0
9,12	Teflon	$\text{SO}_4^{=}$	3.0	0.5
12	Teflon	Na (by AA)	1.0	0.6

\*  $10^{-6} \text{ m}^{-1}$ , which corresponds to an initial absorbance of  $0.253 \pm 0.012$  at a wavelength of 525 nm for the He-Ne laser

### 2.3.2 Results of Pre-study Tests of Substrates

As was briefly mentioned in the introduction, a series of tests to evaluate the performance of the prototype SCAQS sampler were conducted during the three month period preceeding the actual field study. These tests revealed sampling problems that were rectified before the field measurements commenced in June 1987. Specifically the following modifications were made to the prototype sampler:

- o Switching from 1.0  $\mu\text{m}$  pore Gelman nylon filters to ones manufactured by Sartorius (0.67  $\mu\text{m}$  pore) due to quality control problems with the Gelman product (i.e. high variability of blanks and filters that disintegrated during extraction).
- o Increase in etching time for the ammonia denuder from 30 seconds to 5 minutes prior to coating with oxalic acid. This change allowed a heavier coating of oxalic acid which in turn reduced breakthrough of ammonia for the denuder from ~20% to less than 10%.
- o Replacing an oxalic acid impregnated Whatman No. 41 cellulose ester filter with a quartz filter impregnated with oxalic acid. This decreased the breakthrough of fine particulate ammonium from ~30% to less than 1%.
- o Reducing the flowrate through the sodium carbonate (22% by weight) impregnated Whatman No. 541 cellulose fiber filter from a planned 35 lpm to 22 lpm to reduce  $\text{SO}_2$  breakthrough from ~12% to less than 5%. Comparable tests with filters impregnated with 11% (by weight) sodium carbonate solution indicated twice as much  $\text{SO}_2$  breakthrough.
- o Replacing the stilling chamber of the original SCAQS sampler design with a Teflon manifold, and replacing glass inlets with Teflon inlets which reduced nitric acid and ammonia losses from ~60% to less than 5%.
- o Decreasing the flowrate for the polycarbonate filter from 9 lpm to 5 lpm to prevent overloading the filter.

In addition to the above changes made in the original design of the SCAQS sampler based on pre-study tests, two other changes were made to the sampling procedures. First as a result of analyzing the summer  $b_{\text{abs}}$  data from the polycarbonate filters, which often slowed negative values, all filters used for the winter study were analyzed prior to sampling to measure the initial absorbance.

A second change involved sampling with nylon filters. After the first sampling day it became obvious that the particulate loadings were much higher than those observed during the pre-study prototype sampler testing and side-by-side sampler evaluations. The nylon filters were becoming plugged with particles and causing the flow rates to drop considerably (~50%-75%) over the 4-hour to 7-hour sampling periods. Thus, on the second day of sampling, ringed Teflo Teflon filters were deployed as pre-filters in each leg of the SCAQS sampler employing a nylon filter. Thus a Teflon filter and nylon filter sandwiched together were used in legs #1, #3 and #4 to sample ambient gases and particles, and then back in the laboratory both filters were extracted together and analyzed for the species of interest.

It was discovered within the first two weeks of the study that the dynamic blanks for fine ammonium measured on the oxalic acid impregnated quartz filters from the Rubidoux site were very high compared to the other sites; thus, it was decided to see if this "problem" could be minimized. A special experiment was conducted at Rubidoux on July 15, 1987 to evaluate passive absorption of ammonia by these filters. The experiment consisted of exposing an oxalic acid impregnated quartz filter in an open petri dish to the ambient air at Rubidoux during each of the five sampling periods per day. As it turned out the amount of ammonia absorbed by the passive filter blanks represented only 3% to 10% of the actual fine particulate ammonium collected by the collocated field samples. Thus, it was concluded that passive absorption of ammonia by the oxalic acid impregnated filters was unimportant compared to sampling fine particulate ammonium with these filters at the Rubidoux site. Furthermore, since the program plan called for dynamic blanks at each site, it was concluded that any site (or seasonal) dependency for the substrate blanks could be corrected for in the final data compilation. Surprisingly, the ammonia denuders used at Rubidoux did not show higher dynamic field blank levels than those used at other sites even though the ambient levels of ammonia at Rubidoux were the highest measured in the network.



### 3.0 SAMPLING KITS AND SAMPLE COLLECTION LOGISTICS

#### 3.1 SAMPLE KIT PREPARATION

EMSI prepared a total of 800 sample kits for the SCAQS summer and winter study periods. Each kit consisted of an oxalic acid coated denuder tube for sampling ammonia (the ends of which were sealed with parafilm) and 15 filters (each in an individual petri dish) packaged together in a 4" x 6" x 2" plastic "freezer-type" box with a tight fitting lid which was in turn sealed with parafilm. Each kit of filters included:

- o three nylon filters, one each for legs 1, 3 and 4;
- o three Teflo Teflon prefilters, one each for legs 1, 3 and 4;
- o one sodium carbonate impregnated Whatman No. 541 cellulose ester fiber filter for leg 2;
- o one Zefluor Teflon prefilter for leg 2;
- o one oxalic acid impregnated filter for leg 5 (i.e. located behind the ammonia denuder) in a petri dish sealed with parafilm;
- o one Nuclepore polycarbonate filter for leg 6;
- o three pre-fired quartz filters, one each for legs 7, 9 (i.e. as a backup filter behind a Teflon filter) and 10;
- o two pre-weighed Teflo Teflon filters for legs 8 and 11; and
- o two Teflo Teflon filters for legs 9 and 12.

Each ammonia denuder and all petri dishes in the sampling kit, with the exception of the Teflo Teflon prefilters for legs 1, 3 and 4 were labelled with a computer generated dual, piggy-back label which designated both the kit number (e.g. 001 through 800) and the sampling leg number (i.e. 01 through 12). In addition, a computer generated dual, piggy-back label was affixed to the outside of each plastic box containing the filters to designate the kit number. Originally the purpose of the dual piggy-back labels was to have the site technician remove the top portion of each label and affix it to the field data sheet. Instead, the site technicians recorded the label numbers on the

field data sheets, and the top portion of each label was used subsequently by the laboratory technicians to label the samples as they were processed through the laboratory.

The three Teflo Telfon filters (2.0  $\mu$ m pore) in each kit, designated to be used as pre-filters for legs 1, 3 and 4, were added to the sampling kits after the first sampling day indicated that the heavy particulate loadings in the Basin started to plug up the nylon filters (0.65  $\mu$ m pore). These filters were labelled with a handwritten label indicating that they were to be used as a pre-filter in series with the nylon filters. After sampling, both the Teflon pre-filter and the nylon filter pair were loaded back into the original petri dish for the nylon filter and the petri dishes for the Teflon prefilters were discarded.

Sampling kits were prepared in batches of 160 for the summer study and ~120 for the fall study. The former number of kits allowed for three days of sampling at nine sites including blanks and spares, whereas the latter number was sufficient for three days of sampling at six sites plus blanks and spares. A total of four separate shipments of supplies from EMSI to AV were made during the summer study period compared to two for the shorter fall study.

### 3.2 SAMPLE NUMBERING SYSTEM AND DATA SHEETS

Each kit was assigned a three-digit identification number from 001 to 800. Kits numbered 001 through 025 were used by AeroViroment, Inc. to train their site operators on the SCAQS sampler prior to the field study. Kits numbered 026 through 800 were reserved for the field study with instructions to the site operators to use up the sampling kits in numerical order (i.e. oldest sets first). Unused sampling kits were returned to EMSI, repackaged and recycled for reuse with the same original kit number assigned. Site operators were instructed to use the spare sampling substrates shipped to each site when necessary rather than cannabilize existing sampling kits. As it turned out, sample kits 293, 337, 682, and 765-800 were not used in this program. Furthermore, due to

doubling up on sampling for ammonia at San Nicolas Island, the following sample numbers for denuders (i.e. leg #5A) and backup filters (leg #5B) were not used: 130, 132, 134, 136, 311, 313, 317, 318, 320, 322, 323, 325, 327, 328, 336, 337, 385, 387, 389, 391 and 393.

Spares were labelled with a designation indicating filter type and a three digit identification number with a prefix of "S" for spare. With the exception of the pre-weighed Teflon filters and the ammonia denuder tubes, in all cases where a spare filter was used in lieu of the original one included in the sampling kit, the site operator was instructed to discard the damaged filter and reload the exposed spare filter into the labelled petri dish for the damaged filter, thus preserving the sampling scheme for the kit. For the pre-weighed Teflon filters, it was necessary to preserve the labelling scheme for the spares so as to be able to use the recorded tare weight for the specific Teflon filter in calculating the mass of particulate collected by the filter. Later, when the results for these filters (i.e. both mass and elemental composition by XRF) were entered into the data base, the original kit number was reassigned to these samples to preserve the original numbering scheme. [Note: Spare #S-006 used in place of #296 for leg #11; S-007 used in place of #333 for leg #8; S-008 for #283 for leg #8; S-013 for 081 for leg #11; and spare #S-996 for 294 for leg #8.]

In the case of the ammonia denuder tubes, both the original and spare were returned to EMSI along with the data sheet indicating which one was the valid sample. At EMSI the top portion of the dual piggy-back label from the damaged original denuder tube was transferred to the valid spare denuder tube to preserve the kit numbering scheme. Occasionally the site operator at San Nicolas Island used ammonia denuder tubes and oxalic acid impregnated filters incorrectly out of sequence from the rest of the sampling media provided in the sample kits. Thus, filters #389 and #393 were used in place of #390 and #393, respectively. Likewise, the following ammonia denuders were used out of place: 394 for 309, 393 for 310, 384 for 312, 385 for 384, 313 for 386, 311 for 388, 312 for 128, 386 for 129, 309 for 131, 310 for 133, 389 for 135, and 388 for 137. In all

cases the sample labels were "fixed-up" at EMSI to match the corresponding kit numbers prior to analysis to preserve the original kit labelling scheme. [Note: Ammonia denuders #063 and #066 ran for different sampling periods than the rest of sampling media included in these two sampling kits].

Labels for each substrate were assigned a prefix which identified the type of substrate and designated the sampling leg number of the SCAQS sampler. These prefixes were, in order:

- o 01-N1: leg #1 - Nylon Filter #1
- o 02F-Z1: leg #2 front - Zefluor Teflon Filter #1
- o 02B-C1: leg #2 back - Carbonate Impregnated Filter #1
- o 03-N2: leg #3 - Nylon Filter #2
- o 04-N3: leg #4 - Nylon Filter #3
- o 05F-D1: leg #5 front - Ammonia Denuder #1
- o 05-X1: leg #5 - Oxalic Acid Impregnated Filter #1
- o 06-P1: leg #6 - Polycarbonate Filter #1
- o 07-Q1: leg #7 - Quartz Filter #1
- o 08-T1: leg #8 - Teflo Teflon Filter #1
- o 09F-T2: leg #9 front - Teflo Teflon Filter #2
- o 09B-Q2: leg #9 back - Quartz Filter #2
- o 10-Q3: leg #10 - Quartz Filter #3
- o 11-T3: leg #11 - Teflo Teflon Filter #3
- o 12-T4: leg #12 - Teflo Teflon Filter #4

A copy of a field data sheet for the SCAQS sampler listing the collection media by leg number is reproduced in Figure 3-1. This data sheet was filled out by the AV site operators for each sampling period. In addition to filling out the station (i.e. site) name, start and end times, and start and end flowrates on the data sheet, the site operator entered the sampling kit number opposite the space labelled "Tupperware Box #". The I.D. number of any replacement (i.e. spare) filter or denuder tube was entered in the space under "Comments".

# SCAQs Sampler Data Sheet

Station Name: \_\_\_\_\_ Operator's Name: \_\_\_\_\_  
 Start Date: \_\_\_\_\_ Tupperware Box #: \_\_\_\_\_  
 Start Timer/Time: \_\_\_\_\_ / \_\_\_\_\_ Start Temperature: \_\_\_\_\_  
 End Timer/Time: \_\_\_\_\_ / \_\_\_\_\_ End Temperature: \_\_\_\_\_

Sampler Position	Collection Media	Flow Rate(lpm)		Ref Flow+ (lpm)	Sam vol* (m3)	Filter I.D. Number	Comments**
1	Nylon			10-12		1 -N1	
2	Zflour Teflon			22-24		2F-Z1	
	Carbonate			23-27		2B-C1	
3	Nylon			8-10		3 -N2	
4	Nylon			8-10		4 -N3	
5	Oxalic Acid			3 - 5		5 -X1	
6	Polycarbonate			4.5-6.5		6 -P1	
7	Quartz			32-40		7 -Q1	
8	Teflon(plewt)			32-40		8 -T1	
9	Teflon			32-40		9F-T2	
	Quartz			32-40		9B-Q2	
10	Quartz			32-40		10 -Q3	
11	Teflon(plewt)			32-40		11 -T3	
12	Teflon			32-40		12 -T4	
	Denuder			3 - 5		5F-D1	

Vacuum Gauge Readings

Start	End	w/o Filters
1) _____	1) _____	1) _____
2) _____	2) _____	2) _____
3) _____	3) _____	3) _____

+ Reference flow values are approximate and will be qualified for each site. If the measured flow rates are found to be outside of the specified reference flow range, the station operator must inform AV-Monrovia as soon as possible by means of the AV communication number.

\* Sample volume, to be calculated by AeroVironment

\*\* Indicate any problems with sample such as interrupted sample flow or the I.D. number of replacement filters.

FIGURE 3-1. Sample SCAQS data sheet.

### 3.3 SAMPLE COLLECTION LOGISTICS

EMSI prepared all sampling kits for the SCAQS samplers, packaged three days worth of the labelled sampling media, spares and field data sheets into individual containers for each site (i.e. ice chests for tupperware boxes containing filters and sturdy cardboard boxes for ammonia denuder tubes), and shipped these supplies via commercial carrier or an employee of the Air Resources Board to AeroVironment's offices in Monrovia, CA several days in advance of any sampling. AV in turn delivered the supplies to each of the B-sites for the summer and winter sampling periods. In the case of the San Nicolas Island site, two shipments of supplies, each enough for three days, were sent to the site via the station operator.

After sampling exposed and dynamic field blanks (i.e. substrates that were placed in the SCAQS sampler for a short period of time just prior to any actual sampling to simulate handling the substrates in the field) were refrigerated at each site. At the end of each one to three day intensive sampling episode, an AV employee picked up these samples (with the exception of those from San Nicolas Island) and returned them to AV's offices in Monrovia, CA, along with the field data sheets filled out by the site operators and any unused supplies that made up the three day supply originally shipped to each site. At AV an employee calculated the sample volume for each sampling leg based on the start and end times and start and end flowrates and entered the results on the field data sheets. The samples (and any unused supplies) plus copies of the field data sheets were then shipped to EMSI's laboratory located in Camarillo, CA via an employee of the Air Resources Board, where they were logged in by an EMSI employee. Samples from San Nicolas Island were delivered directly to EMSI by AV's site operator on his return trip to AV. The original field data sheets from this remote site were xeroxed at EMSI and then sent to AV in order for an AV employee to calculate sample volumes. Copies of these results were mailed to EMSI within a few days.

After logging in all exposed and unused supplies at EMSI, the exposed samples and dynamic blanks (i.e. for periods prior to actual sampling intensives commencing on Julian days 170, 175, 194, 239, 245, 315, 337 and 344) were sorted by substrate type, inspected and distributed to the different laboratories for analysis along with copies of the field data sheets. Thus, the quartz filters from legs #7, #9B and #10 (i.e. three per sampling kit) were delivered to ENSR for carbon analysis; the Nuclepore polycarbonate filters from leg #6 were mailed to UC Davis for b-absorption measurements; and the pre-weighed Teflon filters from legs #8 and #11 (i.e. two per sampling kit) were mailed to NSI Technology Services Corporation, in Research Triangle Park, North Carolina for XRF analysis after equilibration and gravimetric analysis for mass at EMSI. All other samples were delivered to the EMSI laboratory for analysis. They included: (a) nylon filters plus Teflon pre-filters from legs #1, #3 and #4 for nitrate, (b) carbonate impregnated filters from leg #2 for sulfate (Note: Zefluor Teflon pre-filters from leg #2 were discarded at EMSI), (c) oxalic acid impregnated filters and oxalic acid coated denuder tubes from leg #5 for ammonium, and (d) Teflon filters from legs #9 and #12 for ammonium, chloride, nitrate and sulfate, plus sodium for Teflon filters from leg #12.

Unused supplies were repackaged for shipment to AV and used at the first opportunity. A copy of the chain-of-custody form that accompanied the supplies for the SCAQS sampler is reproduced in Figure 3-2.

Site: \_\_\_\_\_ Denuders: \_\_\_\_\_  
 Ice Chest Number: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 Kit Number: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 Number of Spares: Nylon(N) \_\_\_\_\_ Carbonate(C) \_\_\_\_\_ Quartz(Q) \_\_\_\_\_  
 Teflon(T) \_\_\_\_\_ Zefluor(Z) \_\_\_\_\_ Polycarbonate \_\_\_\_\_  
 Pre-weighed Teflon(T) \_\_\_\_\_ Oxalic(X) \_\_\_\_\_  
  
 Date Packaged at EMSI: \_\_\_\_\_  
 Date Assembler \_\_\_\_\_  
 Date/Time Shipped to AV Central: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_  
 Date/Time Received at AV Central: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_  
 Date/Time Received at Site: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_ Site \_\_\_\_\_  
 Date/Time Shipped to AV Central: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_  
 Date/Time Shipped to EMSI: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_  
 Date/Time Received at EMSI: \_\_\_\_\_  
 Date/Time Received by \_\_\_\_\_  
  

	<u># Used</u>	<u># Unused for Recycling</u>
Kits returned:	_____	_____
Number/type of spares:	_____	_____

CHAIN1.ENV

SCAQS

Figure 3-2. Chain-of-Custody for SCAQS Supplies



#### 4.0 ANALYTICAL METHODOLOGY

Samples from the SCAQS sampler were analyzed by several different laboratories, including:

- o ENSR for carbonaceous aerosol species;
- o UC Davis (and later Radiance Research) for fine particulate b-absorption;
- o NSI Services Technology Corporation for elements by XRF; and
- o EMSI for all other analytes.

Details of each of the analytical methods used for this program are summarized below. The reader is referred to the original standard operating procedures for more information (EMSI, 1987).

##### 4.1 EMSI ANALYTICAL METHODS

For the SCAQS program, EMSI analyzed samples plus field blanks that totaled approximately 5% of the samples from the SCAQS samplers located at the B-sites for the following species:

- o Gas phase species ( $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ) where  $\text{HNO}_3$  is determined by the denuder difference method,  $\text{SO}_2$  on a  $\text{Na}_2\text{CO}_3$ -impregnated filter and  $\text{NH}_3$  from an oxalic acid coated denuder tube;
- o Fine particulate species (mass,  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ) where fine  $\text{NH}_4^+$  is determined both on a Teflon filter plus on an oxalic acid impregnated filter and fine  $\text{NO}_3^-$  is determined both on a Teflon filter plus on a nylon filter;
- o PM-10 particulate species (mass,  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ); and
- o Total nitrate species ( $\text{TSP-NO}_3^-$  plus  $\text{HNO}_3$ ).

The flow of samples and data through the EMSI laboratory is summarized below. Teflon filters are equilibrated and then weighed to determine aerosol mass. Then all filters and oxalic acid coated denuder tubes are extracted and the extracts are stored in a refrigerator prior to analysis. The Teflon filter extracts are first analyzed on a Technicon

Auto-Analyzer for  $\text{NH}_4^+$  and then on a Dionex Ion Chromatograph (IC) for  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , and on an Atomic Absorption Spectrometer for  $\text{Na}^+$ . The nylon filter extracts are analyzed for  $\text{NO}_3^-$  by IC, the oxalic acid coated denuder tube and oxalic acid impregnated filter extracts for  $\text{NH}_4^+$  by the Technicon, and the carbonate impregnated filter extracts for  $\text{SO}_4^{=}$  by IC. All instrumental responses are automatically transferred to EMSI's central computer. The analyst inputs sample ID numbers at a terminal, and concentrations of individual chemical species are calculated in units of  $\mu\text{g}$  per filter.

After a printout of the data is obtained, 10% of all data is rechecked to verify all aspects of the determination. At this time, all quality control data are examined. The printed data are also scanned to catch any outliers. All such outliers are checked carefully to determine if an error has been made in data reduction. After corrections are made in the computer files, a final printout and data are obtained and sent to ENSR, ARB's data manager.

#### 4.1.1 Mass By Gravimetry

Exposed Teflo Teflon filters were re-equilibrated in a temperature and relative humidity controlled clean room at a temperature of  $25 \pm 2^\circ\text{C}$  and a relative humidity of  $45 \pm 5\%$  RH for 24-72 hours prior to reweighing. Then they were weighed on a Mettler microbalance, which had been calibrated with a 2 mg Class M weight, to the nearest microgram. The filter weight was recorded in a logbook opposite the pre-sample tare weight for that specific filter ID number. After each weighing session 10% of all filters in the batch were reweighed by another technician to check that the accuracy of the filter weights met the  $\pm 15 \mu\text{g}$  test. On several occasions they did not; thus another 10% of the filters were reweighed until all re-weights met this criteria. The sample number ID as well as the "begin" and "end" weights for each filter were entered manually into the computer at EMSI by a data clerk within the laboratory operations group.

After EMSI performed a series of validation checks on these samples (e.g. fine mass less than PM-10 mass; positive net mass), the samples were shipped to NSI Technology Services Corporation for XRF analysis for elements.

#### 4.1.2 Extraction of Sampling Media

Basically, the ammonia denuder tubes were rinsed to remove the oxalic acid coating and filters were extracted in different solvents for 20 minutes in an ultrasonic bath. Then the extracts were refrigerated ( $\leq 4^{\circ}\text{C}$ ) prior to analysis for the chemical species of interest.

The extraction medium for the Teflon-nylon pair of filters analyzed for nitrate was a  $0.003\text{-M NaCO}_3/0.0024\text{-M Na}_2\text{CO}_3$  solution which was also the working eluent for the Dionex Ion Chromatograph. 20 ml of this solution was added to a clean 100 ml disposable plastic beaker from a calibrated pipette. The top copy of the dual piggyback label containing the filter number was transferred to the beaker and the Teflon-nylon pair of filters was placed exposed side down in the eluent. The beakers were immediately sealed with a screw-on lid and placed in the ultrasonic bath.

The extraction medium for the Teflon filters analyzed for ions and sodium was 20 ml of deionized water with a trace of ethanol (200  $\mu\text{l}$ ) added to each 100 ml extraction beaker to promote wetting the filter. For the carbonate-glycerine impregnated cellulose ester fiber filters analyzed for sulfate, the extraction medium was 20 ml of 0.06%  $\text{H}_2\text{O}_2$ . For the oxalic acid impregnated filters and oxalic acid coated denuder tubes analyzed for ammonium, the extraction medium was 10 ml of 0.0036-M sodium acetate solution. For the oxalic acid coated denuder tubes, each tube was rinsed four times by drawing the 0.0036-M acetate solution up the tube with a syringe and then releasing it. Each extract from the denuder tubes was stored in a sealed 100 ml beaker in a refrigerator prior to analysis. The extracts from the oxalic acid impregnated quartz filters were filtered with disposable serum separators immediately prior to analysis to remove any quartz fibers.

One reagent blank was prepared for every 30 samples by adding the extraction medium to a 100 ml plastic beaker without a filter. These reagent blanks were taken through the extraction process with the samples to help monitor the reagent blank levels. In addition, laboratory blanks for both the denuder tubes and the filters were extracted and analyzed with exposed samples and dynamic field blanks to monitor filter blank levels.

#### 4.1.3 Ammonium Ion By Colorimetry

Low level ammonium (0.025-5.0  $\mu\text{g/ml}$ ) is analyzed by the Berthelot reaction in which a green colored compound is formed upon addition of an ammonium salt to sodium phenoxide followed by the addition of sodium hypochlorite. Ammonium concentration is then determined spectrophotometrically at 630 nm with a Technicon Auto Analyzer II equipped with a tubular flow cell and a Technicon Model IV autosampler to handle approximately 80 samples per day.

As with all analyses, the instrument response was calibrated with a series of five to seven standards, including a reagent blank, at the beginning and end of each analysis day. A pair of quality control check samples (low level and mid-level) were run after every ten samples to check on recovery efficiency, and approximately five percent of the samples were reanalyzed to measure analytical precision. The analytical response (i.e. peak area) for each sample is recorded automatically by the in-house DEC PDP-11/4 computer via a Hewlett Packard Model 3390A integrator. The printout from the integrator and a stripchart recorder serve as backups to the computer. The Technicon Auto Analyzer requires a 1 ml sample aliquot.

#### 4.1.4 Sulfate, Nitrate and Chloride by Ion Chromatography

A Dionex Model 10 ion chromatograph connected to a Technicon autosampler was used to measure sulfate, nitrate and chloride in the filter extracts. These anions are separated on an anion exchange column (P/N 30827) based on their different affinities for the exchange material which is a polymer coated with quarternary ammonium active sites. After separation, the anions pass through a strong acid fiber suppressor (P/N 35350) which exchanges all cations for  $H^+$  ions. All species are detected as acids by a conductivity meter. The eluent used for this system is a 0.003-M  $NaHCO_3$ /0.0024-M  $Na_2CO_3$  solution. The sulfate and nitrate standards used to calibrate the ion chromatograph ranged from 0.1 to 25  $\mu g/ml$ , and from 0.02 to 5.0  $\mu g/ml$  for the chloride standards. Samples of higher concentration than the highest standards were reanalyzed after appropriate dilution. The ion chromatograph requires a 3 ml sample aliquot.

#### 4.1.5 Sodium by Atomic Absorption

An Instrumentation Laboratories Model 951 atomic absorption spectrophotometer was used to measure sodium in the aqueous filter extracts. The calibration standards for the instrument ranged from 0.05 to 10  $\mu g$   $Na^+$  per milliliter. In the concentration mode on the IL 951, a least squares best fit curve is obtained by the instrument for five calibration standards at the beginning of an analytical run. Concentrations in  $\mu g/ml$  are printed directly onto the instrument's printer and are also automatically transferred to a computer file. The atomic absorption analyzer requires a 2 ml sample aliquot.

#### 4.1.6 Laboratory Quality Control

EMSI has developed an extensive quality control program for the analysis of filters for sulfate, nitrate, chloride, ammonium and sodium. This QC program includes the analysis of special quality control check samples

(QCCS) and the careful examination of the data obtained from these samples. This section discusses the various QC samples and how they are used in evaluating an analytical run.

Standards - A calibration curve consisting of at least four standards is run at the beginning and end of each sample run. For runs of longer than 30 samples, an additional calibration curve is analyzed after each 30 samples. The standards are prepared from stock solutions that are prepared fresh every six months from analytical reagent grade salts for sodium and for ammonium, and ultrapure salts for chloride, nitrate and sulfate. Whenever a new stock is prepared, it is compared to the previous stock to ensure agreement between the two solutions before it is put into use.

Laboratory Quality Control Check Samples (QCCS) - After each standard curve and again after each 10 samples, at least one QCCS is analyzed. These QCCS solutions are prepared from a separate stock solution than the one used to prepare the standards. This stock is prepared from totally separate sources of reagents. These QCCS solutions provide a check on the standards and on the stability of the analysis within the analytical run. The percent recovery for these QCCS samples when compared to the standards must be within 95-105% for sodium, sulfate and nitrate, and 90-110% for chloride and ammonium.

Duplicates - For every 20 samples one extract is analyzed in duplicate. The results from the duplicate analyses are kept in a separate quality control file.

Blanks - For every 30 samples an aliquot of appropriate extraction media is taken through the extraction process to monitor extraction blank levels. For every 30 samples one laboratory filter blank is analyzed to monitor optimum filter blank levels. In addition, dynamic field blanks are also taken through the extraction process to measure actual field blank levels.

Each analytical run is evaluated by examining the results obtained from quality control check samples. If any quality control check sample exceeds the control limits, all data from the analytical run are examined in detail. If more than one quality control sample is out of limits or if any unusual instrument response is observed on the strip chart, all samples are reanalyzed. If only one out of three or four quality control samples is out of limits and all other parameters indicate that the analytical run is normal, the data are accepted. If more than one control is out of limits but they are still within  $\pm 5\%$ , the data are accepted.

#### 4.1.7 External Audits

As part of the SCAQS program, EMSI analyzed a series of spiked filters prepared by Columbia Scientific, Inc. (CSI) and by ENSR for the following analytes:

- o Carbonate impregnated cellulose ester fiber filters for sulfate;
- o Nylon filters for nitrate;
- o Teflon filters for sulfate, nitrate, chloride and ammonium; and
- o Oxalic acid impregnated quartz filters for ammonium.

Recovery on most of these spiked filters was better than 95%. The one exception involved the Teflon filters spiked by CSI for which the recoveries were often less than 80%. This was later traced to the fact that these spiked filters had been placed in the small glassine envelopes for shipping without being completely dry, which resulted in transfer (i.e. loss) of material from the filter to the glassine envelope. Another lesson learned by measuring the recovery of sulfate from carbonate impregnated filters was that one needed to calibrate the system using peak areas rather than peak heights. The results of the laboratory audits by ENSR are documented in their QA report to the ARB (ENSR, 1988).

#### 4.2 ELEMENTAL ANALYSIS BY XRF

The Teflon filters analyzed for mass by EMSI were also analyzed for various elements by a Siemens MRS-3 wavelength dispersive x-ray fluorescence (XRF) spectrometer using a  $10\text{ cm}^2$  Cr-excitation beam. These analyses were conducted by NSI Technology Services Corporation located in Research Triangle Park, North Carolina, under the supervision of Mr. Bob Kellogg (NSI, 1987). The elements quantified included Na, Mg, Al, Si, P, S, Cl, F, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Co, As, I, Br, Sr, Cd, Se, Sc, Bi, Au, Sn, Pt, Sb, W, Ba, Te, La, Mo, Hg and Pb. The instrument is calibrated in units of  $\mu\text{g}/\text{cm}^2$  against thin film standards composed of metallic salts and oxides evaporated on a 47 mm diameter Nuclepore filter purchased from the Micromatter Corporation of Seattle, WA.

#### 4.3 CARBON ANALYSES

Samples were analyzed for particulate levels of organic carbon and elemental carbon by ENSR located in Camarillo, California using ENSR's SOP #115-10. The ENSR carbon analyzer consists of a Dohrmann Model 50 carbon analyzer which employs a dual temperature furnace to volatilize organic carbon at  $525^\circ\text{C}$  and oxidize the elemental carbon at  $850^\circ\text{C}$  from a small aliquot ( $\sim 3\text{ mm}^2$ ) of a quartz filter. The filter aliquot is placed in a platinum sample boat containing manganese dioxide, acidified with dilute HCl and the boat is then advanced into a  $125^\circ\text{C}$  heated zone in a 100% helium carrier gas to remove water, any carbon dioxide or adsorbed organic vapors before being advanced to the  $525^\circ\text{C}$  and later to the  $850^\circ\text{C}$  temperature zones. Carbonaceous material in the sample is oxidized to carbon dioxide which is in turn reduced to methane by an in-line nickel catalyst. The methane is measured with a flame ionization detector which is calibrated by addition of known amounts of potassium acid phthalate (KHP) solution to the sample boat.



#### 4.4 b-ABSORPTION ANALYSES

These analyses were originally conducted by the University of California at Davis under the supervision of Professor Tom Cahill (1987), and then later at Radiance Research under the supervision of Mr. Ray Weiss (1988). Both groups use a method which is basically a modification of the Integrating Plate Method described by Lin et al (1973). In this method, aerosol collected on a 47 mm diameter, 0.4  $\mu$ m pore-size Nuclepore polycarbonate filter is supported on an opal glass plate and placed in a light beam from a helium-neon laser. The opal glass serves to direct light scattered by the particles back to the detector (i.e. a radiometer). The amount of light transmitted through the filter is compared with that transmitted through the unexposed (or blank) filter. The difference in transmission is ascribed entirely to light absorption by the particles.

#### 4.5 QUALITY ASSURANCE

Documentation of precision, accuracy and validity of the data base through a well defined quality assurance (QA) program was an essential component of SCAQS. This QA program was managed by ENSR Consulting and Engineering and implemented with the assistance of the California Air Resources Board (ARB), the South Coast Air Quality Management District (SCAQMD) and Sonoma Technology, Inc. (STI).

ENSR reviewed standard operational and quality control procedures, that were submitted by all study participants, and conducted on-site system audits prior to and during the field studies. The SCAQMD audited the flow rates for the SCAQS samplers at the nine class B sites and found them to be within the acceptable ranges.

Laboratory performance audits were conducted by the ARB and ENSR for ion chemistry at EMSI using spiked filters and sample sets from collocated SCAQS samplers. Results for sulfate, nitrate and ammonium were found to

be satisfactory. The ARB coordinated interlaboratory comparison studies for carbonaceous species, b-absorption, and elemental analysis by X-ray fluorescence due to the difficulty of defining a performance audit procedure for these measurements. The results from the 1986 ARB sponsored Carbonaceous Species Methods Comparison Study have been previously summarized by Countess (1987). For four reference samples of ambient PM-10 particulate material analyzed in triplicate by ENSR, the average coefficient of variation was 2.4% for organic carbon (and for total carbon) and 8.7% for elemental carbon. For these ambient samples, ENSR's values for the elemental carbon versus organic carbon split was in good agreement with the results for the majority of the participating laboratories.

Interlaboratory comparisons for elemental analysis by X-ray fluorescence (i.e. NSI, NEA, DRI and University of Maryland) and for b-absorption (i.e. UC Davis, University of Washington and Radiance Research) indicated a large variability between different laboratories for these measurements. These results are summarized in ENSR's QA report to the ARB (1989).

## 5.0 EMSI DATA REDUCTION AND REPORTING PROCEDURES

The following section describes only EMSI's data reduction and reporting procedures. All other laboratories involved with the SCAQS sampler reported their analytical results (i.e.  $\mu\text{g}/\text{filter}$ ) directly to ENSR, ARB's data manager, whereas AeroVironment reported field data (i.e. sample volumes etc.) to ENSR. ENSR then combined analytical results and sampling data together to calculate blank corrected concentration values (i.e. in units of  $\mu\text{g}/\text{m}^3$ ) for each analyte, and at the same time calculated the overall uncertainty for each measurement. The reader is referred to ENSR final report on data management for the SCAQS study for details concerning these tasks.

### 5.1 LABORATORY DATA MANAGEMENT

In response to the need for rapid and efficient data reduction and reporting, EMSI has developed a disk-based generalized program which has printing, plotting and punched card options. At the start of the project, data pertinent to the project was input in an interactive software mode to create a file structure on disk for the SCAQS project. This generalized program is used for most reduction of analytical data done by the EMSI chemistry laboratory.

Data flow in the EMSI laboratory for this project was as follows. The instrument response for the Dionex Ion Chromatograph, the I.L. Atomic Absorption Spectrometer and the Technicon Auto-Analyzer was automatically transferred to the computer. The chemist then accessed the file which was created, identified the samples, assigned filter ID's, reduced the data, and evaluated the analytical run. This was all performed at a computer terminal. A hardcopy of the instrumental response and the final results were then created and the data were transferred to the data storage files that were previously set up for this project. For backup, a stripchart recorder was also used during all analytical runs in case of computer failure. However, this backup was not needed. A hardcopy of the final analytical results was given to the laboratory manager for

evaluation and approval. Ten percent of all data was checked by hand to ensure the reliability of all data reduction steps. After final evaluation and approval of the data by the laboratory manager, a printout and magnetic tape of the data was submitted to ENSR, ARB's data manager for SCAQS.

## 5.2 CALCULATION OF ANALYTICAL RESULTS

A calibration curve was established in the computer correlating the instrumental response to the analyte concentration for every run. The instrument response for each sample was then compared to the calibration curve to determine its concentration in the extract solution.

The concentration of any given analyte in the extract solution was then converted into the total number of micrograms/filter for that analyte using the following equation:

$$\text{micrograms X/filter} = (\mu\text{g X/ml})(V_E)$$

where, X = Analyte  
V<sub>E</sub> = Volume of Extract

## 5.3 VALIDATION OF DATA

The following procedures were used to validate the analytical data accumulated for the SCAQS program:

- o Any filters designated as invalid by AeroVironment due to damage (i.e. torn or deformed) or improper sampling were flagged in the data base.
- o 100% of input of corresponding EMSI and AeroVironment identification numbers were checked manually.
- o 10% of the values in the data base and all hardcopy data reports were recalculated manually from the raw data. All checks were documented.
- o A series of Level 1 validation checks were performed on the data to check for consistency of data (e.g. fine < PM-10).

- o Raw blank data were checked for outliers (i.e. greater than 3σ above the mean; 99% confidence level).

EMSI identified a small number of samples that were suspect based on sampling problems as identified by the field data sheets. These problems included:

- o sample flow rates out of range
- o missing start and/or end flow rates
- o filter cassette not hooked up
- o filter cassette missing o-ring
- o power failure
- o filter improperly loaded in filter cassette
- o incorrect sample time
- o non-uniform deposit

EMSI notified AeroVironment of these potentially invalid samples in order for AV to flag suspect data in the field data file (i.e. sample volumes) submitted directly by AV to ENSR.

#### 5.4 TREATMENT OF BLANKS

Each laboratory involved with analysis of SCAQS sampler substrates was directed by ENSR, ARB's data manager, to calculate average dynamic blank values for each analyte of interest and provide these results to ENSR. ENSR then used these results to blank correct the data for each sample. The number of dynamic blanks used in this program comprised approximately 10% of the total samples collected.

For the analytes measured by the EMSI laboratory, EMSI reviewed all the dynamic blank data to determine whether there were any site and/or seasonal dependency. Based on simple statistical tests (i.e. comparison

of means), no seasonal dependency was observed for any of the dynamic blanks analyzed by EMSI. However, a site dependency was observed for many of the analytes measured on dynamic blanks from the off-shore, background site located on San Nicolas Island (i.e. site #9). This is clearly illustrated in Table 5-1 (which summarizes the mean and standard deviation for each analyte) where the dynamic blanks for this site are often one-half that observed for the other eight sites located on the mainland.

Furthermore, as illustrated in Table 5-1,  $\text{NH}_4^+$  levels measured on blank oxalic acid impregnated filters (i.e. leg #5B) were lower at Azusa (i.e. site #2) than all other mainland sites, and higher at Rubidoux (i.e. site #8). The site dependency observed for these dynamic blanks is due to either (a) different ambient levels of the analytes of interest at the different sites (e.g. lower at San Nicolas Island; higher  $\text{NH}_3$  at Rubidoux), or (b) different care in handling blanks at each site.

Also included in Table 5-1 are the dynamic blanks that have been identified by EMSI as being outliers at the 99% confidence level. These samples had much higher blank levels than the average levels and are due to either (a) contamination, or (b) a non-negligible ambient air sample that occurred during flow rate checks. These outliers are flagged in the database.

## 5.5 PRECISION OF ANALYTICAL RESULTS

EMSI analyzed approximately 5% of all the samples collected for the SCAQS program in duplicate to evaluate the analytical uncertainty (i.e. precision) for each analyte of interest. The average differences for these replicate analyses are summarized in Table 5-2, expressed both in terms of absolute difference in  $\mu\text{g}$  per substrate and relative percentage difference. Any replicate analysis that was an obvious outlier at the 99% confidence level was eliminated prior to calculating the averages. The absolute differences are consistent with EMSI's analytical detection limits which are shown in Table 5-3; the analytical detection limit is defined as the

DYNAMIC BLANK SUMMARY FOR SCAQS SAMPLER ( $\mu\text{g}/\text{filter}$ )

<u>LEG #</u>	<u>ANALYTE</u>	<u>SITE</u>	<u>N</u>	<u><math>\bar{x}</math> (<math>\mu\text{g}</math>)</u>	<u><math>\sigma</math> (<math>\mu\text{g}</math>)</u>	<u>C.V. (%)</u>	<u>OUTLIERS*</u>
1,3,4	$\text{NO}_3^-$	1-8 9	138 15	4.52 2.15	1.87 0.69	41 32	
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$	1-8 9	50 5	2.06 1.12	1.14 0.23	55 20	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	1-9	56	0.44	0.27	61	#180 (2.5 $\mu\text{g}$ )
5-B	$\text{NH}_4^+$	1,3-7 2,9 8	43 10 8	1.25 0.60 2.14	0.70 0.35 0.76	56 58 36	
8,11	Mass	1-8 9	103 10	41.5 24.3	25.7 24.7	62 102	Leg 8: #282 (194 $\mu\text{g}$ ), #671 (302 $\mu\text{g}$ ), #683 (162 $\mu\text{g}$ )
9,12	$\text{NH}_4^+$	1-8 9	99 10	0.92 0.24	1.04 0.08	113 33	Leg 9: #567 (8.7 $\mu\text{g}$ ) Leg 12: #186 (5.6 $\mu\text{g}$ )
9,12	$\text{Cl}^-$	1-9	113	1.42	0.96	68	Leg 9: #106 (5.8 $\mu\text{g}$ ) Leg 12: #106 (7.8 $\mu\text{g}$ )
9,12	$\text{NO}_3^-$	1-8 9	102 10	5.14 1.18	3.79 0.83	74 70	Leg 9: #595 (18.9 $\mu\text{g}$ ) Leg 12: #595 (19.4 $\mu\text{g}$ )
9,12	$\text{SO}_4^{=}$	1-8 9	100 10	2.59 1.63	1.34 0.72	52 44	Leg 9: #186 (9.1 $\mu\text{g}$ ), #212 (8.3 $\mu\text{g}$ ) Leg 12: #186 (12.6 $\mu\text{g}$ ), #212 (8.8 $\mu\text{g}$ ), and #749 (12.4 $\mu\text{g}$ )
12	Na	1-9	53	1.20	0.85	71	#59 (4.8 $\mu\text{g}$ ), #90 (8.1 $\mu\text{g}$ ), #106 (4.4 $\mu\text{g}$ ), #266 (5.1 $\mu\text{g}$ )

\* Outlier defined as greater than  $x + 3\sigma$  (i.e. 99% confidence limit); in addition Teflon filters #578, #633, #664, and #699 for both legs 9 and 12 were obvious outliers based on extremely high blanks for mass, nitrate and ammonium, indicating that these filters has actually sampled a non-negligible sample of ambient air during flow rate checks.

TABLE 5-2

## AVERAGE DIFFERENCE FOR REPLICATE ANALYSES

<u>LEG #</u>	<u>ANALYTE</u>	<u>N</u>	<u>Average Difference</u>	
			<u>µg/substrate</u>	<u>percentage</u>
1,3,4	$\text{NO}_3^-$	185	0.98	2.1
2-B	$\text{SO}_4^{=}$	34	0.47	2.5
5-A	$\text{NH}_4^+$	52	0.15	1.7
5-B	$\text{NH}_4^+$	52	0.41	6.0
8,11	Mass	133	7.46	2.4
9,12	$\text{NH}_4^+$	169	0.66	2.9
9,12	$\text{Cl}^-$	76	0.06	1.7
9,12	$\text{NO}_3^-$	77	0.90	1.6
9,12	$\text{SO}_4^{=}$	78	0.69	1.2
12	Na	51	0.13	0.8



TABLE 5-3  
ANALYTICAL DETECTION LIMIT  
( $\mu\text{g}/\text{substrate}$ )

<u>LEG #</u>	<u>ANALYTE</u>	<u>DETECTION LIMIT</u>	
		<u>(<math>\mu\text{g}/\text{substrate}</math>)</u>	<u>(<math>\mu\text{g}/\text{m}^3</math>)<sup>*</sup></u>
1,3,4	$\text{NO}_3^-$	0.36	0.14
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$	0.30	0.06
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	0.12	0.12
5-B	$\text{NH}_4^+$	0.12	0.12
8,11	Mass	5.0 <sup>X</sup>	0.60
9,12	$\text{NH}_4^+$	0.24	0.03
9,12	$\text{Cl}^-$	0.30	0.04
9,12	$\text{NO}_3^-$	0.36	0.04
9,12	$\text{SO}_4^{=}$	0.30	0.04
12	Na	0.50	0.06

X Conservative value, since balance reads to  $\pm 1.0 \mu\text{g}$ .

\* Detection limit based on a 4-hour sample.

lowest level detectable based on the specific calibration standards utilized and the actual detector responses. Furthermore, the average percentage differences for all analytes are low; the highest observed percentage difference for replicate analyses was 6%, namely that for  $\text{NH}_4^+$  ion measured on oxalic acid impregnated filters.

It should be pointed out that using replicate analyses of the same sample is not as rigorous a test of overall uncertainty (i.e. precision) based on analyses of duplicate samples from collocated samplers as was possible in the side-by-side pre-study SCAQS sampler evaluations. In those tests, the average percentage difference for these same analytes ranged from 5% to 43% (AeroVironment, 1988a). The analytical results from these replicate analyses were submitted to ENSR where they were combined with the sampling uncertainties for each sample (provided by AV) to calculate an overall uncertainty in the concentration of each analyte.

#### 5.6 LEVEL 1 VALIDATION CHECKS

EMSI performed a series of Level 1 validation checks on the analytical data produced by the EMSI laboratory prior to submitting the raw analytical results (i.e.  $\mu\text{g}/\text{substrate}$ ) to ENSR. These simple validation checks included the following consistency tests which were performed in-house on EMSI's central computer:

- o PM-2.5 mass less than PM-10 mass (i.e. leg #8  $\leq$  leg #11);
- o PM-2.5 analyte concentration less than that for PM-10 fraction;
- o Nitrate for leg #3  $\leq$  leg #4  $\leq$  leg #1;
- o Ammonium for leg #9 (Teflon filter) less than leg #5-B (oxalic acid impregnated filter);
- o Nitrate for leg #9 (Teflon filter) less than leg #3 (nylon filter); and
- o Individual analyte concentration less than mass concentration.

For these tests, EMSI used the original, unvalidated sample volumes provided by AV immediately after each sampling intensive (i.e. one to three day sampling period) to calculate concentrations in units of  $\mu\text{g}/\text{m}^3$  for each analyte. Thus, it is possible that EMSI identified possible inconsistencies when in reality none existed. Less than 1% of the samples failed these Level 1 validation checks. Based on the results of these validation (i.e. consistency) checks, the samples in question were reanalyzed if the differences were significantly greater than that based either on the replicate analyses (see Table 5-2) or on the analytical detection limits (see Table 5-3). If the new analysis changed the result such that the sample now met the consistency check, this value was substituted for the original value and was included in the data base that was submitted to ENSR. If the new analysis did not affect the results of the consistency check, the original value ( $\mu\text{g}/\text{substrate}$ ) was left in the data base, since ENSR planned to repeat these Level 1 consistency checks based on blank corrected concentration data (i.e.  $\mu\text{g}/\text{m}^3$ ).

In the case of filters analyzed for mass (i.e. Teflon filters in legs #8 and #11), the consistency checks often identified transcription errors which were easy to correct based on reweighing of the end weight for each suspect sample. However, in several instances the consistency checks identified the possibility of a transcription error in the pre-sample weight which were not possible to correct. This problem was encountered with the following filters:

- o Leg #8: 197 (213  $\mu\text{g}$ , not 10,213  $\mu\text{g}$ ); 432 (425  $\mu\text{g}$ , not -9,575  $\mu\text{g}$ )
- o Leg #11: 392 (256  $\mu\text{g}$ , not 10,256  $\mu\text{g}$ ); 469 (718  $\mu\text{g}$ , not -9,282 $\mu\text{g}$ ); 555 (mass # - 7,137  $\mu\text{g}$ ; filter was torn)

In addition to these five samples, the following filters failed the consistency check even after reweighing for mass (i.e. leg #8  $\leq$  leg #11): 121, 141, 147, 150, 191, 196, 329, 389, 470, 486, 531, 532, 548, 684, 685, 689, 690, 694, and 731. We believe that it is possible that

the site operator may have inadvertently switched the filters for legs #8 and #11 in loading the SCAQS samplers (especially for samples #'s 684, 685, 690, and 694) and then placed them back in the correctly labelled petri dishes. The XRF results for these filters should be used to test this hypothesis.

## 5.7 DATA FLAGS

The following flags were used by EMSI to identify blanks and suspect data for the SCAQS samplers based on either (a) field data sheet entries, or (b) observations made by EMSI's sample log-in technician for all SCAQS sampler substrates:

- o Flag = 1: Blank
- o Flag = 2: Damaged (eg. torn; bent)
- o Flag = 3: Contaminated (eg. dropped; dirty)
- o Flag = 4: Non-uniform deposit
- o Flag = 5: Missing sample
- o Flag = 6: Ammonia denuder heater defective
- o Flag = 7: Flowrate problems (eg. leak; low flow rate; power failure)
- o Flag = 8: Incorrect filter, or mislabelled sample

The samples that were flagged with these eight different flags are summarized below in Tables 5-4 through 5-11.

In addition to the flags listed above, EMSI provided ENSR, ARB's data manager, a list of flags for suspect data based on Level 1 validation checks. This latter list included flags for the following conditions:

- o Below analytical detection level
- o Analytical problem
- o High blank (i.e.  $>3\sigma$  above mean blank value)

TABLE 5-4

FLAGGED SCAQS FILTERS: FLAG = 1 (BLANKS)

DAYS: 170, 175, 194, 239, 245, 315, 337, 344

SAMPLE #'S

026	210	567
032	212	578
042	218	583
046	229	595
058	234	599
059	245	617
074	250	633
080	261	639
090	266	664
097	277	671
106	282	683
108	294	699
122	298	705
128	309	716
138	314	732
145	471	738
156	483	749
158	503	765
170	518	
180	519	
186	535	
199	551	

TABLE 5-5

FLAGGED SCAQS FILTERS: FLAG = 2 (DAMAGED)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
1	$\text{NO}_3^-$	050, 268, 502	Teflon prefilter #268 damaged
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$		
3	$\text{NO}_3^-$	502	
4	$\text{NO}_3^-$	044, 396, 427, 532, 669, 756	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	122	#122 doesn't look coated
5-B	$\text{NH}_4^+$	299	
8	mass	054, 067, 111, 200, 201, 265, 320, 329, 374, 401, 440, 445, 457, 461, 462, 480, 508, 533, 556, 660, 698	
9	ions	---	
11	mass	075, 113, 126, 150, 160, 180, 197-199, 201, 211, 315, 336, 378, 421, 422, 429, 436, 441, 444, 449, 454, 459, 470, 493, 514, 538, 554, 555, 587, 600-602, 608, 611, 649, 713	
12	ions	605, 746	

TABLE 5-6

FLAGGED SCAQS FILTERS: FLAG = 3 (CONTAMINATED)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
1	$\text{NO}_3^-$	046, 253, 294, 299, 338, 578, 633, 664, 699, 704, 716	
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$	026, 097, 179, 183, 338, 683, 687	
3	$\text{NO}_3^-$	170, 184, 240, 461, 467, 578, 633, 664, 671, 699, 764	
4	$\text{NO}_3^-$	216, 257, 261, 498, 578, 633, 664, 699, 764, 765	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	503, 633	
5-B	$\text{NH}_4^+$	152, 166, 199, 446, 451, 669	
8	mass	078, 165, 627, 649	
9	ions	044, 071, 750, 760	
11	mass	053, 100, 131, 154, 348, 543, 750	
12	ions	049, 284, 387, 431, 522, 617, 649	

TABLE 5-7

FLAGGED SCAQS FILTERS: FLAG = 4 (NON UNIFORM DEPOSIT)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
5-A	NH <sub>3</sub> as NH <sub>4</sub> <sup>+</sup>	063, 066	Denuder ran different period than backup oxalic acid filter



TABLE 5-8

FLAGGED SCAQS FILTERS: FLAG = 5 (MISSING SAMPLE)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
1	$\text{NO}_3^-$	433, 462, 478, 717, 750	
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$		
3	$\text{NO}_3^-$	227, 430, 439, 462, 478 717	
4	$\text{NO}_3^-$	462, 478, 539, 717	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	128, 181, 229-233, 302, 354, 440, 447, 449, 473, 558	
5-B	$\text{NH}_4^+$	467, 484, 574	
8	mass	273	

TABLE 5-9

FLAGGED SCAQS FILTERS: FLAG = 6 ( $\text{NH}_3$  DENUDER HEATER INOPERABLE)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	049, 081, 095, 353, 424, 526, 542, 636, 733, 734, 745	
5-B	$\text{NH}_4^+$	049, 081, 095, 353, 424, 526, 542, 636, 733, 734, 745	

TABLE 5-10

## FLAGGED SCAQS FILTERS: FLAG = 7 (FLOW RATE PROBLEMS)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
(a) <u>Low Flow Rates</u>			
1	$\text{NO}_3^-$	027, 029, 031	
3	$\text{NO}_3^-$	028, 029, 031, 062, 065, 098, 146	
4	$\text{NO}_3^-$	028, 029, 031, 062, 065, 069, 098, 124	
	+		
5-A/5-B	$\text{NH}_4$	557	
(b) <u>Not Hooked Up</u>			
3	$\text{NO}_3^-$	241, 448	
4	$\text{NO}_3^-$	056, 241, 306, 437, 448, 520	
5-A	$\text{NH}_3$ AS $\text{NH}_4^+$	241, 398	
5-B	$\text{NH}_4^+$	241, 398	
8	mass	241	
9-A	ions	241	
11	mass	241	
12	ions	241	
(c) <u>Pump Shut Off Prematurely</u>			
1-8	All	711	
8-12	All	099, 584	
11	mass	585	
12	ions	585	
(d) <u>Miscellaneous Flow Problems</u>			
3-5	All	213	Missing start flow
9-A	ions	755	Air leaks around filter

TABLE 5-11

FLAGGED SCAQS FILTERS: FLAG = 8 (INCORRECT FILTER MEDIA USED)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
1	$\text{NO}_3^-$	371, 381	
2-A	$\text{SO}_2$ as $\text{SO}_4^{=}$	547, 668-670, 693-742	Filters not impregnated
3	$\text{NO}_3^-$	064, 326-329, 381	
4	$\text{NO}_3^-$	181, 326-329, 381	

- o PM-2.5 > PM-10 for any analyte
- o  $\text{NH}_4^+$  on Teflon filter >  $\text{NH}_4^+$  on oxalic acid filter
- o  $\text{NO}_3^-$  on Teflon filter >  $\text{NO}_3^-$  on nylon filter
- o Leg #3 > leg #4 for  $\text{NO}_3^-$
- o Leg #4 > leg #1 for  $\text{NO}_3^-$
- o Leg #3 > leg #1 for  $\text{NO}_3^-$
- o Analyte > mass

The flags for suspect data included in the SCAQS sampler data volumes attached as appendices to this report are by no means limited to those listed above. Each laboratory involved with analysis of these samples was free to add additional flags to these basic lists.

A list of suspect sample results based on analytical problems (tentatively Flag = 21) appears in Table 5-12. Unfortunately, these problems (e.g. integrator malfunction; sample misidentified) were discovered at a relatively late date by the EMSI laboratory supervisor after the Level 1 validation checks had been completed. At this point in time the sample extracts had either been used or discarded, thereby preventing reanalysis of these samples.

Blanks that appear at the 99% confidence level to be outliers (i.e. greater than the mean plus 3 standard deviations) are identified in Table 5-13 (and are tentatively identical with a Flag = 25). Samples that failed the Level 1 consistency checks are identified in Table 5-14 (and are tentatively assigned a Flag = 31).

TABLE 5-12

FLAGGED SCAQS FILTERS: FLAG = 21 (ANALYTICAL PROBLEMS)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'s</u>	<u>Comments</u>
1	$\text{NO}_3^-$	058, 199, 261, 492-495	
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$	446, 610	
3	$\text{NO}_3^-$	074, 080, 106, 180, 245, 492-495	
4	$\text{NO}_3^-$	074, 106, 108, 158, 229, 492-495	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	135, 137, 310, 384, 386, 388, 392	
5-B	$\text{NH}_4^+$	452, 459	
9-A	$\text{NH}_4^+$	264, 436, 438, 468, 471, 472, 495-497, 503, 504, 518, 620, 671, 683, 727	
12	$\text{NH}_4^+$	215, 338, 396-405, 498, 513, 575-577, 648	
12	Na	026, 148, 221, 226, 270, 616, 698, 707	

TABLE 5-13

FLAGGED SCAQS FILTERS: FLAG = 24 (HIGH BLANK)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
1	$\text{NO}_3^-$	--	
2-B	$\text{SO}_2$ as $\text{SO}_4^{=}$	--	
3	$\text{NO}_3^-$	--	
4	$\text{NO}_3^-$	--	
5-A	$\text{NH}_3$ as $\text{NH}_4^+$	180	
8	mass	282, 578, 633, 664, 671, 683, 699	
9-A	$\text{NH}_4^+$	567, 578, 633, 664, 699	
9-A	$\text{Cl}^-$	106, 578, 633, 664, 699	
9-A	$\text{NO}_3^-$	578, 595, 633, 664, 699	
9-A	$\text{SO}_4^{=}$	186, 212, 578, 633, 644, 699	
11	mass	578, 633, 664, 699	
12	$\text{NH}_4^+$	186, 578, 633, 664, 699	
12	$\text{Cl}^-$	106, 578, 633, 664, 699	
12	$\text{NO}_3^-$	578, 595, 633, 664, 699	
12	$\text{SO}_4^+$	186, 212, 578, 595, 633, 664, 699, 749	
12	Na	026, 059, 090, 106, 266	Suspect #026 switched with #226 in lab.

TABLE 5-14

FLAGGED SCAQS FILTERS: FLAG = 31 (FINE &lt; PM-10)

<u>Leg #</u>	<u>Analyte</u>	<u>Sample #'S</u>	<u>Comments</u>
8 vs 11	mass	121, 141, 147, 150, 191 196, 329, 389, 470, 486, 531, 532, 548, 731	
8 vs 11	mass	197, 392, 432, 469	Suspect transcription errors
8 vs 11	mass	555	11-555 was torn
8 vs 11	mass	684, 685, 689, 690, 694	Suspect filters switched in field
9 vs 12	NH <sub>4</sub> <sup>+</sup>	194, 252, 334, 347	



## 6.0 REFERENCES

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